Fate and behaviour of flupyrsulfuron-methyl in soil and aquatic systems†

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Abstract: The environmental fate of [^{14}C]flupyrsulfuron-methyl, a sulfonylurea herbicide, was investigated in soil and aquatic systems. The major degradative pathways in both systems were contraction of the sulfonylurea bridge followed by intramolecular rearrangement (at pH > 7) or sulfonylurea bridge hydrolysis (at pH < 7). Hydrolysis was a first-order reaction and was pH- and temperature-dependent. Flupyrsulfuron-methyl was degraded rapidly at 25°C in pH 5, 7 and 9 sterile buffers with half-lives of 44, 12 and 0.42 days, respectively. At pH 7 and 9, sulfonyl bridge contraction and rearrangement was the major degradative mechanism; at pH 5 the sulfonylurea bridge was also hydrolysed. Unique photodegradation products were formed at pH 5 and pH 7 but, in general, hydrolysis was faster than photolysis at all three pH values.

Aerobic aquatic metabolism involved biphasic degradation of the herbicide (DT_{50} 3–6 days), degradation being faster in the aerobic aquatic systems than in sterile buffers. Degradation in aerobic soils was rapid, both in the laboratory (DT_{50} 8–26 days) and in the field (DT_{50} 6–11 days, DT_{90} 35–123 days). In laboratory studies the rate of degradation in soil reduced with decreasing temperature (rate at 10°C half that at 20°C) but was unaffected by soil water content (50% vs 70% maximum water holding capacity). The compound was degraded in flooded anaerobic soils (DT_{50} 33 days).

Flupyrsulfuron-methyl was weakly absorbed to soils, there being a linear relationship between adsorption and soil organic carbon content. Following application of [^{14}C]flupyrsulfuron-methyl to bare field soil the radioactivity moved little, with very little radioactivity found in soil below 60 cm from the surface.

Keywords: degradation; dissipation; environmental fate; flupyrsulfuron-methyl; sulfonylurea herbicides; adsorption; hydrolysis.

1 INTRODUCTION

Flupyrsulfuron-methyl [methyl 2-(4,6-dimethoxypyrimidin - 2 - ylcarbamoylsulfamoyl) - 6 - trifluoro - methylnicotinate monosodium salt] is the active ingredient in Lexus® Herbicide used to control grasses and broadleaf weeds in cereals. This new sulfonylurea herbicide is applied post-emergence to crops, using ground-directed broadcast sprays at a maximum rate of 12 g AI ha^{-1}. Its mode of action and selectivity[1,2] have been discussed elsewhere.

Studies were instigated to investigate its metabolism in soil and aquatic environments, degradation, dissipation in the field, hydrolysis, aqueous photolysis and mobility in soil. The compound is formulated for practical use as the monosodium salt but the ^{14}C-labelled acid form of flupyrsulfuron-methyl was used in the majority of the environmental fate studies. Conversion of the acid-form to the salt is pH-dependent and reversible, being governed by the acid dissociation constant pKa (pKa = 4.9). At pH > 5, which is the environmentally relevant pH area, the salt will predominate. For simplicity, the ^{14}C-material used in this work is referred to as flupyrsulfuron-methyl, irrespective of the ambient pH at which it was used.

2 MATERIALS AND METHODS

2.1 Chemicals

The radiolabelled test compounds [*pyrimidine*-2-^{14}C]- and [*pyridine*-2-^{14}C]-flupyrsulfuron-methyl were synthesized at New England Nuclear Products (Boston MA, USA); they had radiochemical purities of >95% and specific activities of 1.52 and 1.56 MBq mg^{-1}, respectively. Non-labelled samples

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of flupyrsulfuron-methyl and potential degradation products were synthesized at DuPont Agricultural Products (Wilmington, DE USA). All other chemicals used were of reagent grade, or better, and solvents were of HPLC grade. The water solubility of flupyrsulfuron-methyl at 25°C is 0.063 and 0.60 g litre^{-1} at pH 5 and 7, respectively (Cooke LA DuPont Internal Report AMR 2477-92, 1994, unpublished). Since the compound is unstable at pH 9, no solubility data are available for this pH.

The compound is not volatile, the vapor pressure being $<10^{-8}$ Pa at 25°C (Cobranchi DP and Schmuckler ME, DuPont Internal Report AMR 3165-94, 1995, unpublished).

2.2 Test soils and sediments

Fresh field soils and sediments were obtained for the laboratory studies and stored moist at 4°C. The microbial activity of samples used in soil degradation and water/sediment studies was determined by incubating test portions on selective media (agar) and counting the number of micro-organism colonies which developed. Each test soil was screened through a 2-mm sieve prior to analysis for soil characteristics (Table 1). Dissipation was monitored at three field sites in Europe and the USA. The soil samples from these experiments were also screened through a 2-mm sieve prior to analysis of soil characteristics (Table 2). Sediments were centrifuged to remove as much water as possible and the moist residue screened through a 2-mm sieve prior to being characterized (Table 3).

2.3 Radioassay

For laboratory and field studies, total radioactivity in aqueous solutions or extracts was quantified in scintillation cocktail (Special Scintillator M131, Canberra Packard, Pangbourne, UK) using a liquid scintillation counter (Philips Model PW4700, Philips NV, Eindhoven, The Netherlands) and external standards. Radioactivity in extracted soil or sediment solids was quantified by combustion of the sample in a Harvey Biological Oxidizer (Model OX500, OX400 or OX300; RJ Harvey Instrument Co, Hillsdale, NJ, USA) followed by liquid scintillation counting (LSC) of the trapped [^{14}C]carbon dioxide in Oxysolve C-400 (Zinsser Analytic, Maidenhead, UK), Oxosol C14 (National Diagnostics, Atlanta, GA,

Table 1. Characterization of soils used in laboratory studies[a]

Source	*Somersham sandy loam*	*Probstei loam*	*Nambsheim sandy loam*	*Le Verniol silt loam*	*Evesham 3 clay loam*	*Speyer 2.2 loamy sand*
Country of origin	UK	Germany	France	France	UK	Germany
Sand (0.05–2.0 mm) (%)	57	42	54	22	30	84
Silt (0.002–0.05 mm) (%)	27	43	37	61	32	11
Clay (<0.002 mm) (%)	16	15	9	17	38	5
Organic carbon (%)	1.5	1.3	0.7	1.3	1.9	2.3
pH[b]	7.4	6.1	7.6	6.4	7.1	5.8
CEC (mequiv 100 g^{-1})	10.2	0.5	7.6	5.6	2.6	6.2

[a] Soil analyses performed by Soil Survey and Land Research Centre (Silsoe, Bedfordshire, UK).
[b] pH measured in water.

Table 2. Characterization of soils at the field sites[a]

Field site	*Alconbury*	*Nambsheim*	*Newark, Delaware*
Country of origin	UK	France	USA
Sand (0.05–2.0 mm) (%)	36	74	42
Silt (0.002–0.05 mm) (%)	32	15	43
Clay (<0.002 mm) (%)	32	11	15
Organic carbon (%)	1.9	1.1	1.9
pH[b]	7.3	7.8	6.1
CEC (mequiv 100 g^{-1})	22.6	9.8	0.5

[a] Soil analyses performed by Soil Survey and Land Research Centre (Silsoe, Bedfordshire, UK) or Harris Laboratories (Lincoln, NE, USA).
[b] pH measured in water.

Source	Cooch's Bridge, Delaware	Brandywine River, Delaware
Country of origin	USA	USA
Water characterization[a]		
Dissolved organic carbon (mg liter^{-1})	6.2	3.1
Hardness (mg equiv $CaCO_3$ liter^{-1})	41	55
Total Kjeldahl nitrogen (mg liter^{-1})	1.1	0.5
Total phosphorus (mg liter^{-1})	<D.L[b]	<D.L
pH	7.24	7.46
Sediment characteristics[c]		
sand (0.05–2.0 mm) (%)	37.2	93.2
silt (0.002–0.05 mm) (%)	47.2	6
clay (<0.002 mm) (%)	15.6	<D.L
organic matter (%)	0.9	0.3
pH[d]	6.3	7.3
CEC (mequiv 100 g^{-1})	5	2.4
Total nitrogen (mg kg^{-1})	515	246
Phosphorus (mg kg^{-1})	9	5
Texture	Loam	Sand

[a] Water analyses performed by Midwest Laboratories, Inc (Omaha, NE, USA).
[b] Less than detection limit.
[c] Sediment analyses performed by Harris Laboratories (Lincoln, NE, USA).
[d] Measured in water.

Table 3. Characterization of water and sediments

USA) or Carbon 14 Cocktail (RJ Harvey Instrument Co).

2.4 Analytical methods

Aqueous samples and extracts of soils and sediments were analyzed by HPLC using a Zorbax Rx-C18 column (4.6 × 250 mm) and a gradient elution with water (adjusted to pH 3 with phosphoric acid; Solvent A) + acetonitrile (Solvent B) at a flow rate of 1.5 ml min^{-1}. The gradient composition was (minutes/%B): 0/2, 2/2, 25/70, 32/100, 35/2 and 45/2 (Method 1). For all hydrolysis and photolysis samples incubated at 20°C (except the pH 9 samples), Method 2 was used incorporating Solvent A as 0.1 mM ammonium formate + formic acid (0.03% by volume). For those hydrolysis samples incubated at 30°C, and for all pH 9 hydrolysis and photolysis samples, Solvent A comprised aqueous formic acid (0.05% by volume) (Method 3). HPLC analyses were done on a Waters, Varian 5000 or Shimadzu SCL-6A HPLC system. For HPLC with radioactive samples, a fraction collector was used to collect the eluant (at 1-min intervals), followed by LSC analysis; for non-radioactive samples, detection was by UV at 254 nm wavelength. Identification of radiolabelled species was based on comparison of retention times with those of reference compounds. TLC analyses were performed on silica gel plates (Kieselgel 60 F_{254}, 0.25 mm thickness). Mobile phases were ethyl acetate + hexane + acetic acid (80 + 20 + 1, by volume; Method A), diethyl ether + hexane (9 + 1, by volume, Method B) and ethyl acetate + methanol + acetic acid (90 + 10 + 0.5, by volume, Method C). Radiolabelled species were located on TLC plates by radiography with X-ray film, identification being by comparison with reference compounds.

2.5 Soil extraction methods

Soil and sediment samples (50–100 g) in 250 ml centrifuge bottles were extracted with acetonitrile + pH 6.5 0.1 M sodium phosphate buffer (3 + 1, by volume). The bottle was immersed in an ultrasonic bath for 15 min then shaken on a wrist-action shaker for 15 min, after which it was centrifuged (2500 rev min^{-1}; 15 min); this process was repeated at least three times. The supernatant solutions were decanted and the residue from the final treatment was shaken with acetonitrile for 5 min, the mixture centrifuged and the supernatant added to the combined supernatants from the previous treatments. The volume of the combined solution was measured and replicate samples (1.0 ml) were analyzed by LSC to determine total extractable radioactivity. The bulk of the solvent was removed and the residual solution was either filtered through a 0.2-μm filter or centrifuged to remove soil particles and the solution was then subjected to HPLC analysis for flupyrsulfuron-methyl and its degradation products. This procedure gave >95% extraction efficiency for flupyrsulfuron-methyl in unaged soils and sediments; data were not corrected for recovery. The residual solids after extraction were air-dried, homogenized and samples (3 × 1 g) were combusted and analyzed by LSC. The

limit of detection for radiochemical methods was $0.3\,ng\,g^{-1}$ for HPLC analysis and $0.1\,ng\,g^{-1}$ for combustion.

The total radioactivity in aqueous solutions was measured by LSC (three replicate determinations); aqueous samples were filtered or centrifuged to remove particulate matter and analyzed by HPLC.

2.6 Calculation of DT_{50} and DT_{90} values in soil and sediment studies

Kinetic analyses involved using the equation that gave the best fit to the data. Pseudo-first-order kinetics were assumed to apply in laboratory soil metabolism studies in order to allow calculation of $t_{1/2}$ values; the amount remaining of each radiolabelled form of flupyrsulfuron-methyl was averaged. Data were subjected to linear regression analysis of ln(mean% residual flupyrsulfuron-methyl) versus time, using the Graphwriter 2 (1987) computer software package (Lotus Development Corporation, Cambridge, UK), results which allowed determination of the rate constant (k).

Non-linear kinetics were assumed in the water/sediment study and in the field dissipation studies, the rate constant being calculated using the equation described by Gustafson and Holden[3]

$$\ln C = \ln Co - \mathrm{A}\ln(1 + \mathrm{B}t) \qquad (1)$$

where A and B are scaling factors. The best-fit line was determined by non-linear regression using Deltagraph® Professional software (Deltapoint Inc, Monterey, CA, USA). DT_{50} and DT_{90} (time to reach 50 and 90% dissipation, respectively) values were calculated using the equations

$$\mathrm{DT}_{50} = [0.5^{-1/\mathrm{A}} - 1]/\mathrm{B} \qquad (2)$$

$$\mathrm{DT}_{90} = [0.1^{-1/\mathrm{A}} - 1]/\mathrm{B} \qquad (3)$$

2.7 Control of bias in sampling

The two radiolabelled forms of flupyrsulfuron-methyl, at the pyrimidine and pyridine rings, respectively, served as duplicates at each sampling point. For laboratory studies the entire sample from an individual vessel was analyzed at each time. Variation between the duplicate samples (radiolabel) was generally $<10\%$. For the field dissipation studies, the soil cores were taken randomly across the test plot. Sub-plots to be sampled at intervals were chosen using a random number generator. Field samples were homogenized thoroughly before subsampling for analysis.

2.8 Hydrolysis and aqueous photolysis rate determination

Rates of hydrolysis and aqueous photolysis were determined by monitoring the disappearance of the two radiolabelled forms of flupyrsulfuron-methyl in 0.1 M aqueous buffer solutions (acetate, phosphate and borate for pH 5, 7 and 9, respectively). The buffer solutions and all apparatus used, were autoclaved (121°C, $15\,lb\,in^{-2}$; 15 min) prior to use and aseptic techniques were used throughout the study.

Stock solutions of the radiolabelled test substances in acetonitrile were sterilized by filtration through a 0.2-μm filter. Stock solution (25 μl) in sterilized buffer (2.5 ml) gave a nominal concentration of 20 μg test substance ml^{-1} in each sterilized glass vessel. Duplicate samples (one for each label type) were prepared for each sampling time for each buffer. For the hydrolysis study, these solutions were incubated in the dark for up to 30 days at 20°C or up to 16 days at 30°C.

Samples for the aqueous photolysis studies were prepared as above and were irradiated in a Suntest® unit (WC Heraus, Hanau, Germany) fitted with a xenon arc light source and filters to cut off light of <290 nm wavelength. The spectral energy distributions of the light source and of natural sunlight were measured using a Minimate-2 Model 181A monochromator linked to a model 730 radiometer (Glen Creston Instruments Ltd, London, UK). Samples were irradiated for up to 15 days at 20°C. Data for percentage parent molecule remaining with time allowed determination of the rate constant as discussed above. To relate the intensity of the xenon lamp to natural sunlight, it was assumed that daily radiation intensity from the sun is $c75\%$ of the peak intensity over a 12-h period, in contrast to the constant and continuous intensity of radiation from the Suntest® unit. The equivalent days of latitude 52°N summer sunlight (D) received by each test sample were calculated using the equation

$$D(\mathrm{days}) = (h \times r)/(0.75 \times 12) \qquad (4)$$

where h = duration (hours) or irradiation in the Suntest apparatus; r = ratio of intensity of Suntest radiation to natural sunlight at latitude 52°N; 0.75 is the correction for diurnal variation of natural sunlight and 12 is a conversion factor of hours to days. The values of r for different positions within the Suntest apparatus varied from 1.45 to 2.02 and were used to correct rate constants for sunlight equivalents, the corrected values being used to determine half-life values.

At each sampling time, samples were analyzed directly by LSC and reverse-phase HPLC (Method 2 or 3) to determine the total amount and distribution of [^{14}C]flupyrsulfuron-methyl and its degradation products. Structures of the degradation products were confirmed by co-chromatography with authentic reference standards using HPLC and TLC (Method B or C). In general, only those compounds relating to $>10\%$ of the applied radioactivity (%AR) were identified.

2.9 Aerobic aquatic metabolism

Aerobic aquatic metabolism studies were performed in water and sediment obtained from Cooch's Bridge (loam sediment) and Brandywine Creek (sand sediment), both in Delaware, USA, using both radiolabelled forms of flupyrsulfuron-methyl. Samples of sediment (25 g dry weight equivalent) with an overlayer of water (100 ml) were placed in plastic vessels and a solution of radiolabelled test substance (in methanol) was added to each vessel so that the final concentration of test substance was *c*0.1 μg ml^{-1} in the aqueous layer. The containing vessels were attached to a trapping system consisting of 1 M potassium hydroxide (to trap carbon dioxide) and ethylene glycol (to trap organic volatiles) and the vessels were also attached to a vacuum manifold to allow humidified air to be drawn through the system. The vessels were incubated in the dark at *c*20°C for up to 120 days.

Samples taken at intervals were centrifuged to allow separation of water and sediment layers and the water layer was analyzed (in triplicate) by LSC and HPLC (Method 1). The traps were analyzed at each sampling interval by LSC (triplicate aliquots). The sediment was extracted (as described above) and the extract was analyzed by HPLC. The identities of the degradation compounds were confirmed by co-chromatography with authentic standard compounds.

2.10 Aerobic and anaerobic soil metabolism

Aerobic soil studies were performed in a variety of soils, using the two radiolabelled forms of flupyrsulfuron-methyl. For the aerobic breakdown pathway study, samples of moist Somersham soil (equivalent to 100 g dry weight) were placed in glass vessels and the moisture content was adjusted to 50% of the maximum water-holding capacity (MWHC) by adding distilled water.

Stock solutions of the two test materials in methanol were diluted with water (3 + 1, by volume) to give dosing solutions. These solutions (2 ml) were applied as evenly as possible to the surface of the soil in the test vessel, which had been allowed to equilibrate in the dark at 20°C for seven days before dosing. For the aerobic study, the vessels were attached to a vacuum manifold to allow air to be pulled through the system and the vessels were also attached to a series of traps, the first containing ethyl digol, the second 1 M potassium hydroxide and the third ethanolamine + 2-ethoxyethanol (1 + 3, by volume); vessels in the anaerobic tests were not under vacuum. The soil moisture content was monitored and adjusted at weekly intervals and soil samples were taken at appropriate intervals during the 365-day incubation period. Soils were extracted and the soil and extracts were analyzed as described above (Method 1). The trapping solutions were monitored by LSC (and the solutions replaced) at each sampling or at around four-week intervals.

In order to identify the products of degradation in soil, vessels containing Probstei soil (100 g dry weight equivalent) were treated with [*pyridine*-^{14}C] flupyrsulfuron-methyl at the high dose of 20 μg ml^{-1}. The dosing solution contained both labelled and non-labelled compound (*c*3 and *c*12 mg, respectively) in methanol (3.75 ml) diluted with water to 12 ml, portions of which (2 ml) were applied evenly to the soil surface. Treated soils were adjusted to 50% MWHC and incubated in the dark at 20°C for 100 days. The degradation products were characterized by GC/MS; in general, those products accounting for $\leqslant$10% of the total radiolabel were not identified.

Rate of degradation was studied in four soils (Nambsheim, Le Verniol, Evesham 3 and Probstei) incubated at both 50% and 70% MWHC. Otherwise, experimental methods and conditions were as for the previous experiments. The soils were incubated in the dark and the soil moisture content was monitored regularly and adjusted at weekly intervals. Analysis was as described previously, the extract being examined using HPLC Method 1.

Anaerobic degradation was studied in Somersham soil. Soil samples were treated as for the aerobic route studies and initially incubated under aerobic conditions for *c*18 days. Anaerobic conditions were then initiated by flooding the soil with distilled water and purging with nitrogen + carbon dioxide (99 + 1, by volume). Samples were incubated under these anaerobic conditions at *c*20°C for up to 100 days. Volatile radioactive products were trapped and analyzed as described for the aerobic study. Samples were extracted and analyzed as described above and the identities of degradation products were confirmed by co-chromatography with authentic standards, by HPLC and by normal-phase TLC (Method A).

2.11 Sorption by soil

Batch equilibrium studies were performed using [*pyridine*-2-^{14}C]flupyrsulfuron-methyl applied to each of five soils ranging from sandy loam through silt loam to clay loam (Table 1). Freundlich isotherm experiments for both adsorption and desorption involved stock solutions in 0.01 M calcium chloride with concentrations between 0.01 and 1.01 μg ml^{-1} prepared from a *c*1 mg ml^{-1} solution in acetonitrile. To measure adsorption in soil, the soil sample (10 g dry weight) and test solution (20 ml) were shaken in the dark at 25°C for 8 h and then centrifuged. The supernatant solution was assayed by LSC. Of the four replicates for each soil receiving the highest concentration of flupyrsulfuron-methyl, two were stored overnight at *c*4°C prior to the desorption phase of the study. The remaining two samples were used to determine the extent of degradation of flupyrsulfuron-methyl that had occurred during the adsorption phase. For these two samples, the aqueous supernatant solutions described above were com-

Compound[a]	*HPLC retention times (min)*			*TLC R_f values*		
	Method 1	*Method 2*	*Method 3*	*Method A*	*Method B*	*Method C*
flupyrsulfuron-methyl	24.0	24.0	24.0	0.33	0.04	0.73
1	21.5	21.5	NA[b]	0.48	0.43	0.80
2	23.8	NA	22.5	NA	0.11	0.72
3	NA	NA	13.0	NA	0.48	NA
4	17.3	16.5	17.0	0.57	NA	0.78
5	22.3	NA	18.5	NA	NA	0.40
6	30.0	NA	29.5	NA	0.63	0.84
7	17.4	17.0	17.0	0.23	0.05	0.72
8	14.5	14.0	NA	0.10	0.03	0.59
9	20.5	NA	20.5	NA	NA	NA
10	10.0	NA	NA	NA	NA	NA

Table 4. Typical HPLC-UV retention times and TLC values of flupyrsulfuron-methyl and its degradation products

[a] See Figs 1 and 3.
[b] Not applicable.

bined and analyzed by LSC and HPLC Method 1.

The soils were extracted, by immersing the vessels in an ultrasonic bath at ambient temperature for up to 30 min, up to four times with either acetonitrile + 0.1 M ammonium carbonate (3 + 1, by volume; Somersham or Le Verniol) or acetonitrile + 0.1 M sodium phosphate (3 + 1, by volume; Nambsheim, Evesham 3 and Speyer 2.2). Extracts and soils were separated by centrifugation and the extracts from the replicates for each soil were combined. A sub-sample of the combined extract (40 ml) was concentrated under reduced pressure and the concentrate was diluted to 10 ml with water prior to analysis by LSC and HPLC Method 1. The extracted soils were air-dried, weighed and three replicate samples of each soil were combusted to measure residual radioactivity.

For the desorption phase experiments, the soils remaining from treatments with the highest concentration of flupyrsulfuron-methyl after extraction and centrifugation were shaken for eight hours with fresh 0.01 M calcium chloride in the dark, after which the supernatant liquid was removed and the soils were stored overnight at *c*40°C. The samples were then submitted to another 8-h desorption treatment with fresh calcium chloride solution. The individual liquid extracts were assayed by LSC and the residual soils were extracted and analyzed as described for the adsorption phase (using a 1.0 ml injection volume for HPLC). Sorption data were analyzed using the Freundlich Equation, the slope ($1/n$) and coefficient of sorption (K) being obtained by least squares regression of log C_e(Concentration of parent in solution at equilibrium) against $\log(x/m)$ (concentration of parent in soil). The K values were adjusted for organic carbon content K_{oc}) using the equation

$$K_{oc} = [K/(\%OC)] \times 100 \qquad (5)$$

2.12 Dissipation in field soil

Bare-soil field dissipation trials were conducted at Alconbury, UK; Nambsheim, France and Newark, DE, USA, using the two radiolabelled forms of flupyrsulfuron-methyl at a rate of 15 g AI ha^{-1}. The Newark site plot size was 91 × 335 cm, divided into 103 cm^2 sub-plots and those in Europe were 225 × 335 cm, with 100 cm^2 sub-plots.

In the USA, the application solution consisted of labelled (1.5 mg) and unlabelled (3.0 mg) flupyrsulfuron-methyl dissolved in buffered water (pH 7.0; 200 ml) to which was added the appropriate formulation inert materials for a 50DF (wettable granule) formulation, whereas in Europe the labelled compound (2.8 mg) was dissolved in buffered water (pH 7.0; 110 ml) and the formulation inerts were added. All application solutions were prepared immediately before spraying. They were applied evenly to the bare soil using hand-held plant misters, which were rinsed with buffer solution after the first application and this rinsate was then also applied to the soil in the plot. Applications were as follows: in May 1994 at the Newark site (spring application), in December, 1993 at Alconbury (autumn application) and, to separate plots, in April 1994 (spring application) and in December 1993 at Nambsheim (autumn application).

Triplicate soil cores were taken at each sampling time from randomly selected sub-plots, sub-plots being sampled only once during the study, using a multi-stage soil coring device (Concord Researchers' Special, S & G Soil Services, Bedfordshire, UK or Concord Environmental Equipment, Hawley, MN, USA). The first sample (0–15 cm) was taken, followed by a second core (15–90 cm) where feasible, all cores being collected in acetate sleeves. The lower cores were sectioned, using a hacksaw, prior to analysis. The three cores from the same depth and treatment for each soil were combined and mixed. Soil samples were extracted and analyzed as described previously, degradation products being characterized by co-chromatography with authentic standards.

3 RESULTS AND DISCUSSION

There was no significant decline in microbial counts from soils and sediments over the course of the studies.

Representative times for HPLC and R_f values for TLC are presented in Table 4.

3.1 Hydrolytic and aqueous photolytic degradation

The rate of hydrolysis of flupyrsulfuron-methyl was dependent on pH, being faster at alkaline pH (Table 5), and also increased with increase in temperature. The degradation pathway of the parent compound in sterile buffers is summarized in Fig 1. At pH 7 or 9 the major degradation product was 1-(4,6-dimethoxy-2-pyrimidinyl)-7-(trifluoromethyl)pyrido [2,3-d]pyri-midine-2,4(1*H*,3*H*)-dione (**1**, Fig 1). At pH 5 there were four major degradation products: compound **1** and methyl 2-[(aminocarbonyl)(4,6-dimethoxy-2-pyrimidiny)aminol]-6-trifluoromethyl-3-pyridinecarboxylate (**2**) were formed as a result of sulfonylurea bridge contraction followed by internal

Table 5. First-order rate constants and half-lives for the degradation of flupyrsulfuron-methyl in sterile aqueous buffer at 20°C and 30°C[a]

pH	Rate constant (day^{-1})			Half-life (day)		
	Hydrolysis	Photolysis[b]	Photolysis[c]	Hydrolysis	Photolysis[c]	Hydrolysis + photolysis[c]
5	0.0159 (0.0927)	0.0062	0.00147	44 (7.5)	470	40
7	0.0592 (0.163)	0.0928	0.0207	12 (4.2)	33	8.7
9	1.64 (7.18)	0.600	0.129	0.42 (0.097)	5.4	0.39

[a] 30°C data in parentheses and performed for hydrolysis only.
[b] Not corrected for natural sunlight equivalents.
[c] Corrected to natural sunlight equivalents.

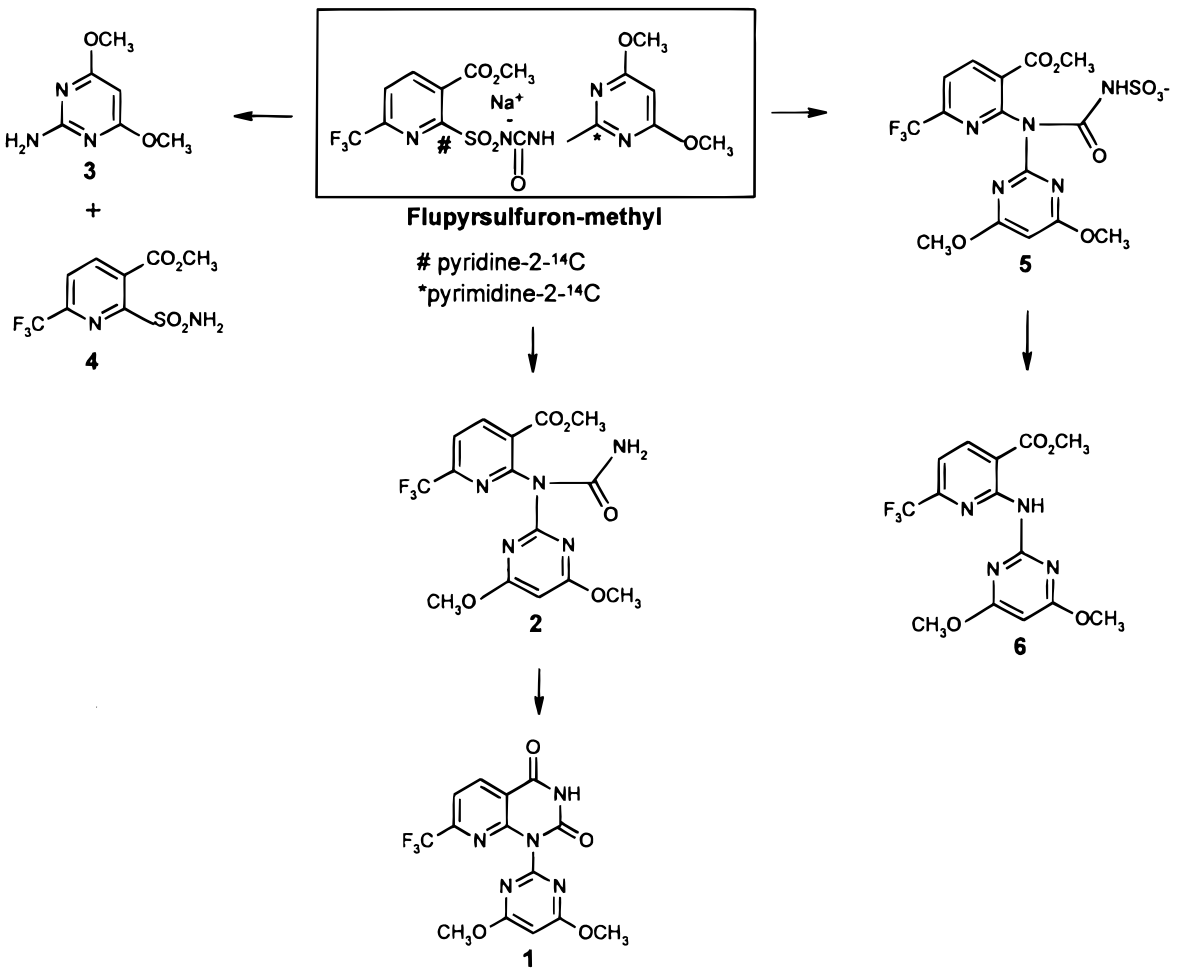

Figure 1. Degradation of [^{14}C] flupyrsulfuron-methyl in irradiated and non-irradiated aqueous systems.

Table 6. Non-linear regression parameters describing the dissipation of flupyrsulfuron-methyl in water and sediment

Parameter	*Cooch's Bridge loam*		*Brandywine river sand*	
	Water phase	*Total system*[a]	*Water phase*	*Total system*[a]
DT_{50} (days)	6	6	3	3
DT_{90} (days)	36	46	20	25
Scaling factor A	1.76	1.28	1.21	0.940
Scaling factor B	0.075	0.110	0.286	0.417
Correlation Coefficient (r^2)	0.955	0.923	0.943	0.921

[a] Combined water and sediment.

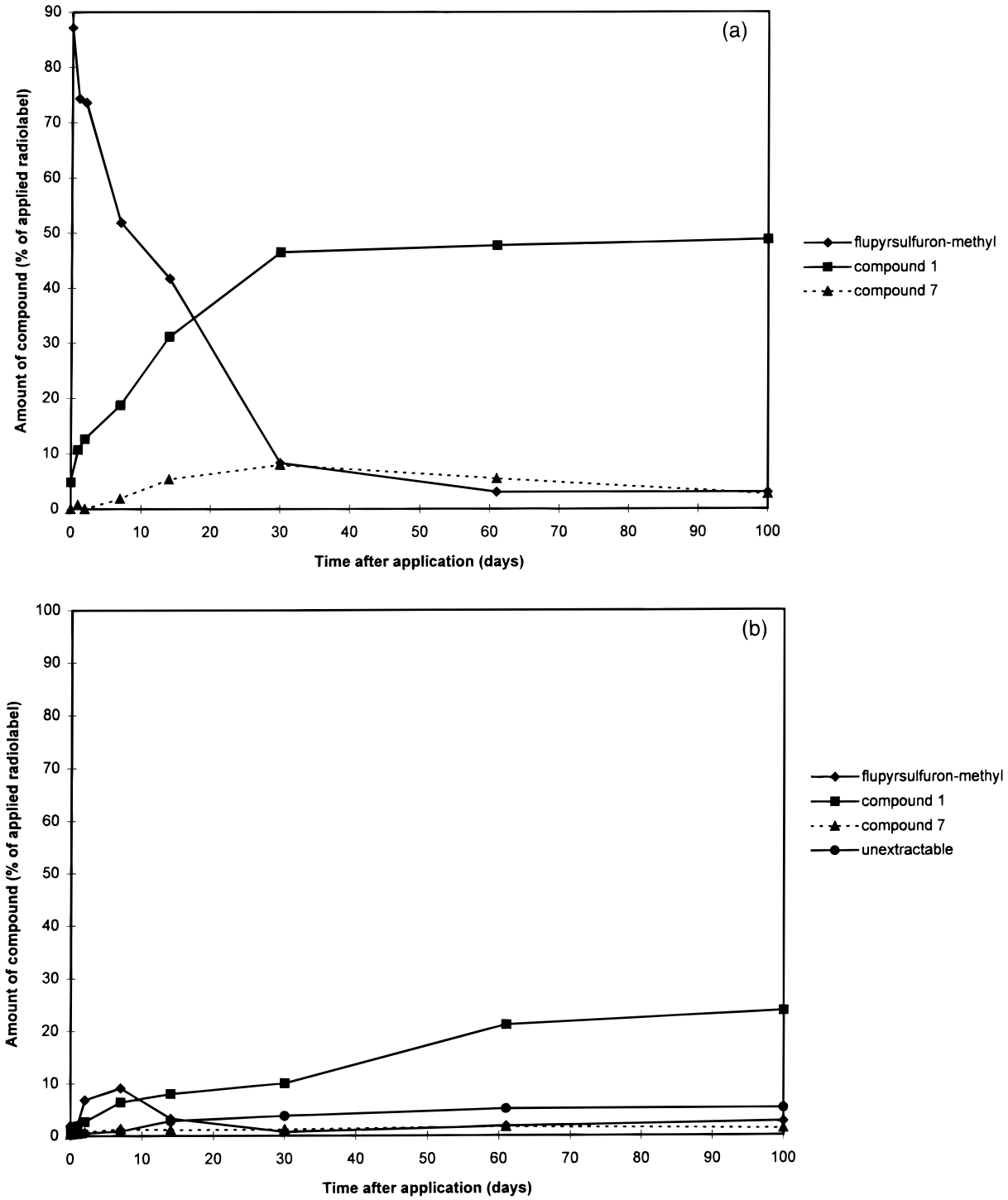

Figure 2. Distribution of [^{14}C] flupyrsulfuron-methyl and its degradates in the Cooch's Bridge water/sediment system. (a) Water phase, (b) Sediment phase.

rearrangement of the molecule (Fig 1) while 4,6-dimethoxy-2-pyrimidamine (**3**) and methyl 2-(aminosulfonyl)-6-(trifluoromethyl)-3-pyridinecarboxylate (**4**) resulted from hydrolysis of the sulfonylurea bridge.

Hydrolysis of flupyrsulfuron-methyl was faster than photolysis (Table 5). The rates of photolysis were also pH-dependent, being higher at higher pH. Some products or degradative pathways occurred only in irradiated solutions (Fig 1). At pH 5, **1** and **2** were formed in both irradiated and non-irradiated solutions, although they were only minor components of the former. However, sulfonylurea bridge cleavage did not occur in irradiated solutions at this pH. At pH 7, the irradiated parent compound underwent rearrangement of the sulfonylurea bridge giving methyl 2-[(4,6-dimethoxy-2-pyrimidinyl)-[(sulfoamino)carbonyl]amino]- 6 -(trifluoromethyl)-3-pyridinecarboxylate (**5**). Loss of the sulfonylurea group from **5** yielded methyl 2-[(4,6-dimethoxy-2-pyrimidinyl)amino]- 6 -(trifluoromethyl)-3-pyridinecarboxylate (**6**). The major degradation product at pH 7 was compound **1** in non-irradiated solutions, but it accounted for a maximum of only *c*5% in irradiated solutions.

Compound **1** was the major component of both irradiated and non-irradiated solutions at pH 9.

3.2 Aerobic aquatic metabolism

Flupyrsulfuron-methyl was degraded rapidly in both water/sediment systems (Table 6), the distribution of parent and degradation products being shown in Fig 2. The major degradation products in the water from both systems were **1** and 1-(4-hydroxy-6-methoxy) 2-pyrimidinyl-7-(trifluoromethyl)pyrido [2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (**7**; Fig 3). In the sediment, the major degradation product was **1**. Unextractable residues reached a maximum of 2.8–6.7% AR, while [^{14}C] carbon dioxide evolved ranged from 1.3 to 4.2% AR. Recovery of radioactivity was >90%. Degradation was faster in the aerobic aquatic systems than in sterile buffers.

3.3 Aerobic and anaerobic soil metabolism

The aerobic soil studies showed the existence of three main degradative pathways depending on the soil pH (Fig 3). At pH > 6.6, contraction and ipso rearrangement of the sulfonylurea bridge predominated, giving **1** which, in turn, underwent *O*-demethylation to form **7** and 1-(4,6-dihydroxy-2-

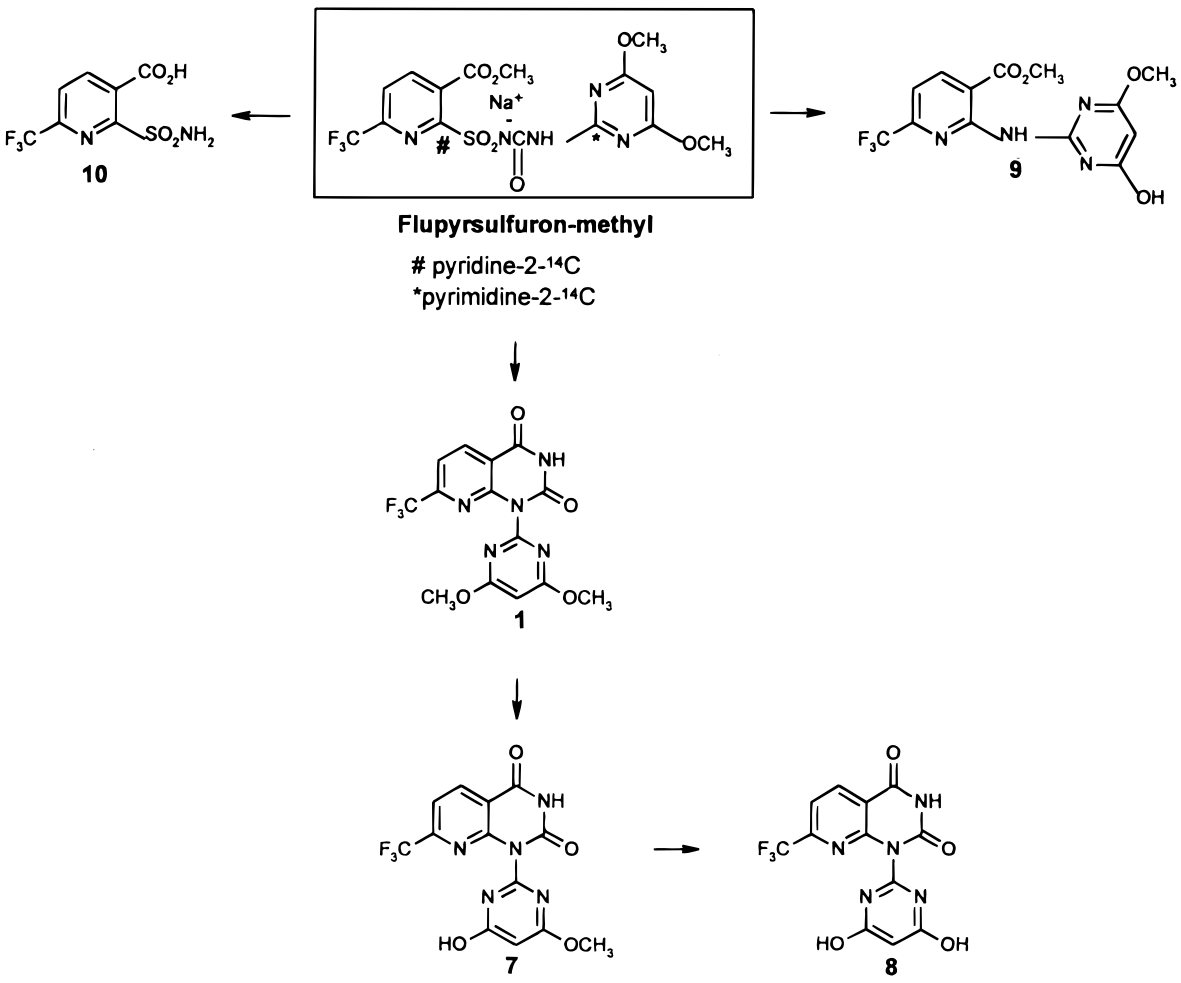

Figure 3. Degradation of [^{14}C] flupyrsulfuron-methyl in soil and sediment systems.

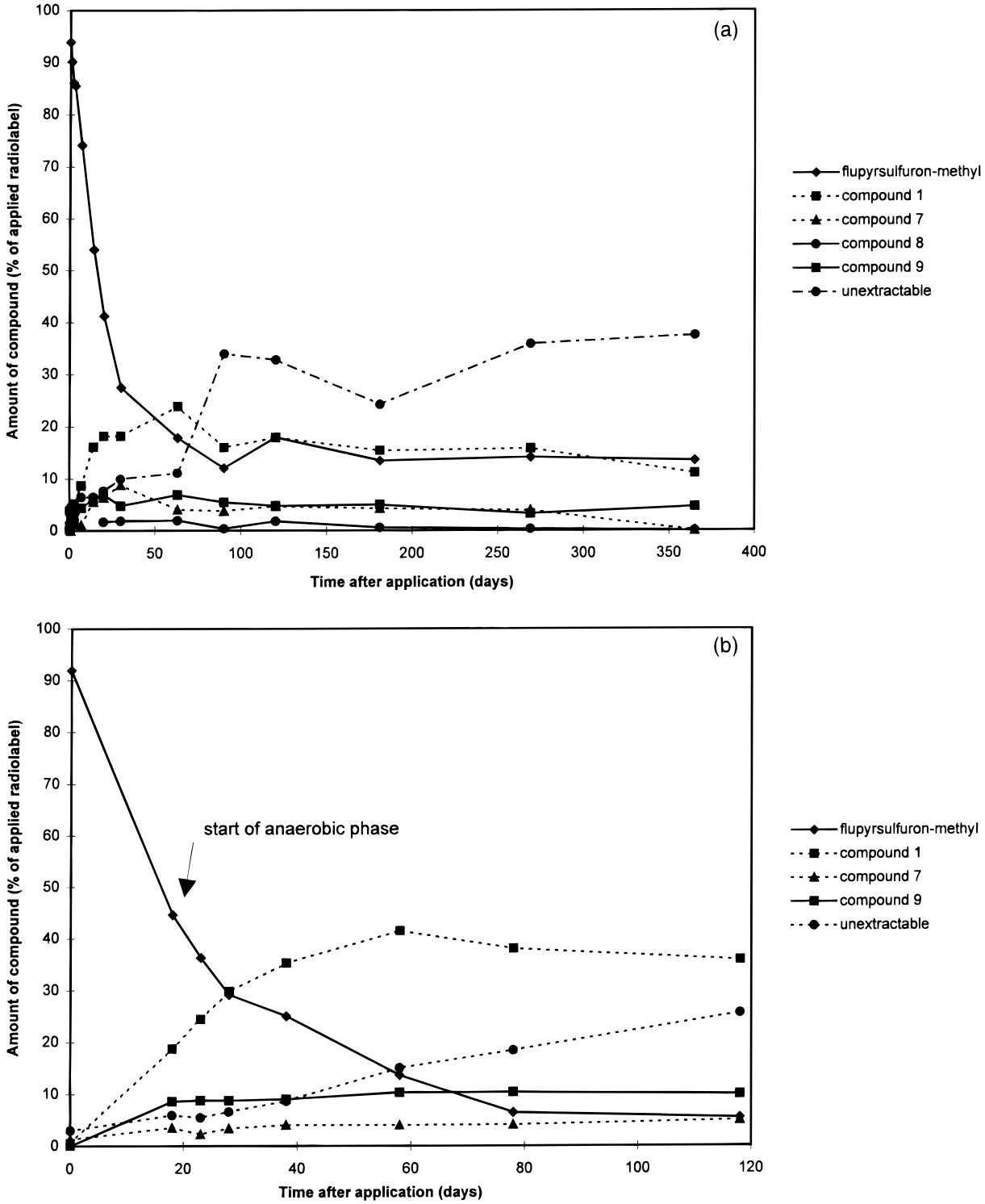

Figure 4. Distribution of ^{14}C-residues of flupyrsulfuron-methyl in (a) aerobic and (b) anaerobic (after 18 days of aerobic incubation) soil studies performed in Somersham sandy loam soil.

pyrimidinyl)-7-(trifluoromethyl)pyrido [2,3-*d*]pyrimidine-2,4[1*H*,3*H*]-dione (**8**) and bridge contraction to form methyl 2-[(4-hydroxy-6-methoxy-2-pyrimidinyl) - amino] - 6 - (trifluoromethyl) - 3 - pyridinecarboxylate (**9**). In more acidic soils, a significant pathway was cleavage of the sulfonylurea bridge to form 2-(aminosulfonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid (**10**; maximum of 32.3% AR at 100 days in Probstei soil), in addition to rearrangement to **1** (**1** reached a maximum of 27.3% in 30 days). There were no significant differences in the metabolic pathways for aerobic and anaerobic conditions (Fig 4). The difference in degradation pathway between pH > 6.6 and more acidic pH values also occurred in the aqueous hydrolysis studies. Flupyrsulfuron-methyl was degraded rapidly in soil under aerobic conditions (Table 7), with a range of DT_{50} values from nine to 24 days. There was no obvious correlation between soil characteristics or moisture content and degradation, which was

Soil	Moisture (%) (MWHC)	Incubation temperature (°C)	DT_{50} (days)
	Aerobic incubation		
Somersham sandy loam	50	10	58
	50	20	26
	70	20	24
Nambsheim sandy loam	50	20	8
	70		8
Le Verniol silt loam	50	20	16
	70		18
Evesham 3 clay loam	50	20	10
	70		9
Probstei loam	50	20	16
	70		16
	Anaerobic incubation		
Somersham sandy loam	50	20	31

Table 7. Rates of degradation of flupyrsulfuron-methyl in aerobic and anaerobic soils

Soil	Soil pH	Organic Carbon (%)	Adsorption			Desorption		
			K_a	K_{oc}	1/n	K_d	K_{oc}	1/n
Somersham sandy loam	7.4	1.5	0.22	15	0.86	0.21	14	0.47
Nambsheim sandy loam	8.8	0.7	0.13	19	0.85	0.11	16	0.23
Le Verniol silt loam	7.4	1.3	0.29	22	0.92	0.26	20	0.51
Alconbury clay loam	8.1	1.9	0.44	23	0.91	0.39	21	0.54
Speyer 2.2 loamy sand	5.8	2.3	0.50	22	0.88	0.42	18	0.74

Table 8. Adsorption/desorption on soil

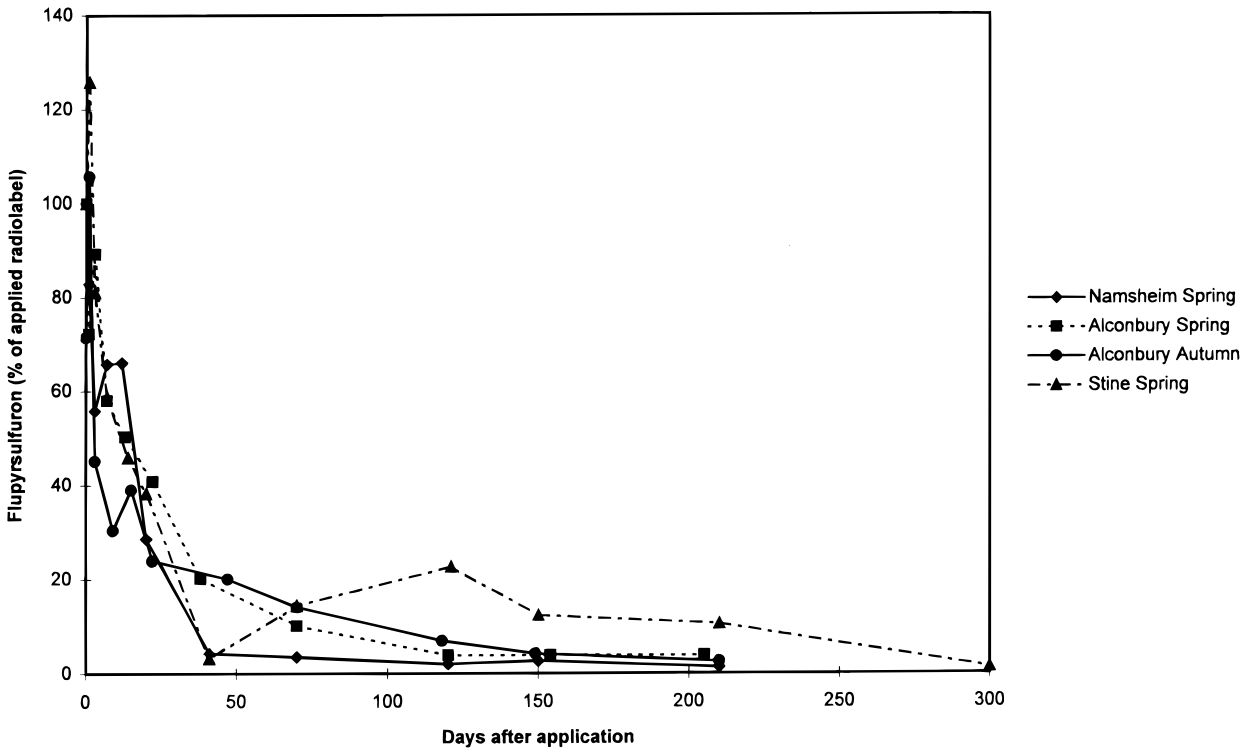

Figure 5. Dissipation of [^{14}C] flupyrsulfuron-methyl under field conditions.

Table 9. Non-linear regression parameters describing the decline of flupyrsulfuron-methyl in field soils after autumn or spring applications

Parameter	*Newark Delaware Spring*	*Alconbury, UK Autumn*	*Alconbury, UK Spring*	*Nambsheim, France Autumn*
DT_{50} (days)	6	10	11	6
DT_{90} (days)	123	104	77	35
Scaling factor A	0.602	0.92	1.50	1.49
Scaling factor B	0.365	0.110	0.0521	0.105
Correlation Coefficient (r^2)	0.742	0.832	0.859	0.898

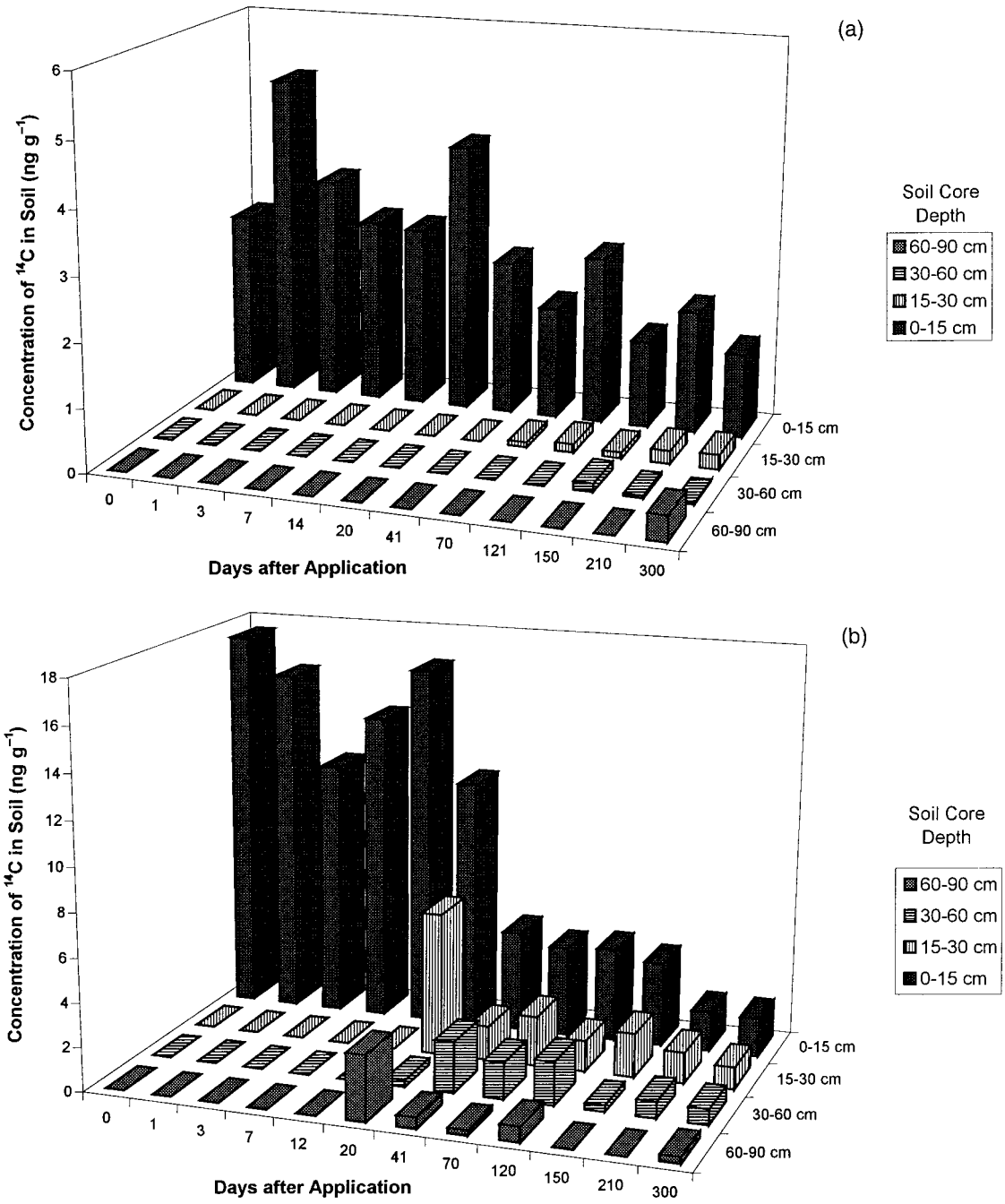

Figure 6. Distribution of ^{14}C-residues in soil after application of flupyrsulfuron-methyl to bare field soils at (a) Delaware, USA and (b) Nambsheim, France field sites.

approximately twice as fast at 20°C than at 10°C. Degradation was slightly slower under anaerobic than under aerobic conditions in the Somersham soil (DT_{50} = 31 days).

3.4 Sorption to soil

There was a linear correlation between the Freundlich adsorption constants and the organic matter content of the soils (Table 8). While flupyrsulfuron-methyl was found to be weakly adsorbed to all the soils, its actual leaching potential will be influenced by several factors including soil type, application rate and rate of degradation.

3.5 Dissipation in field soils

[^{14}C]Flupyrsulfuron-methyl was degraded rapidly in soil under field conditions, exhibiting biphasic degradation kinetics (Fig 5). There was no significant seasonal variability in degradation rate, that at the Alconbury site being essentially the same after the autumn and spring application (Table 9). At the Delaware, USA, site, both **1** and **7** were present in appreciable concentrations (<10% AR) but only **1** was detected in such concentration at the other field sites. Unextractable residues in the top horizon of soil ranged from a maximum (average of the two radiolabelled forms) of 4.2% (Nambsheim) to 34% (Delaware) of the applied radioactivity. The extremely small amount of radioactivity detected in soil below 60 cm indicates little potential for flupyrsulfuron-methyl or its degradation products to leach into groundwater (Fig 6).

4 CONCLUSIONS

Flupyrsulfuron-methyl, as the [*pyrimidine*-2-^{14}C]- and [*pyridine*-2-^{14}C]-compound, has been shown to degrade rapidly in soil, water and sediment, but photolytic degradation is slower. The degradative pathways have been elucidated and the rate of degradation is shown to be pH-dependent. Degradation pathways were similar under aerobic and anaerobic conditions and degradation occurred faster in field than in laboratory studies. The rapid dissipation of the parent compound in soil makes its accumulation in the environment unlikely.

The lack of movement of flupyrsulfuron-methyl or its degradation products to >60 cm below the soil surface, together with a low use rate and interception by crop plants, all suggest little potential for the parent compound or its degradation products to reach ground water.

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